(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 0 913 402 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
06.05.1999 Bulletin 1999/18

(51) Int. Cl.[6]: **C07F 7/18**

(21) Application number: **97118191.2**

(22) Date of filing: **20.10.1997**

(84) Designated Contracting States:
AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE
Designated Extension States:
AL LT LV RO SI

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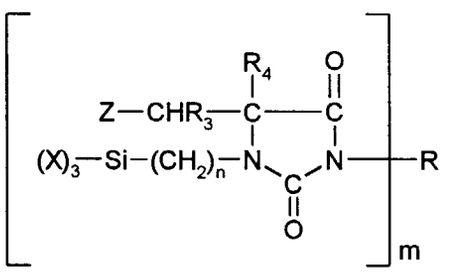
(54) Compounds containing alkoxysilane groups and hydantoin groups

(57) The present invention relates to compounds containing alkoxysilane and hydantoin groups and corresponding to the formula



(I)

wherein

X represents identical or different organic groups which are inert to isocyanate groups below 100°C, provided that at least one of these groups is an alkoxy group,

Z represents $COOR_1$ or an aromatic ring,

R represents the residue obtained by removing the isocyanate groups from an organic monomeric polyisocyanate or a polyisocyanate adduct of an NCO content from 5.1 to 60%,

R_1 represents an organic group which is inert to isocyanate groups at a temperature of 100°C or less,

R_3 and R_4 are identical or different and represent hydrogen or organic groups which are inert to isocyanate groups

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at a temperature of 100°C or less,

n is an integer from 1 to 8 and

m has an average value of 2 to 6.

The present invention also relates to the use of these compounds for the preparation coatings or adhesives.

Description

Background of the Invention

Field of the Invention

[0001] The present invention relates to compounds containing alkoxysilane groups and hydantoin groups and to their use as coatings or adhesives.

Description of the Prior Art

[0002] Hydrolyzable organofunctional silanes are key components for linking conventional polymer chemistry with silicone chemistry. Compounds of technical importance for this purpose are in particular those corresponding to the formula

$$(RO)_3Si\text{-}(CH_2)_3\text{-}Y$$

wherein

R is an alkyl group and

Y is a functional group.

[0003] Such compounds contain both hydrolyzable silyl group, OR which crosslink by „silane polycondensation" in the presence of moisture, and other functional groups, Y, which enable them to be chemically linked to conventional polymer materials. (See e.g., Agnew. Chem. 98 (1986) 237-253).

[0004] Hydrolyzable functional silanes corresponding to the above formula in which the functional group Y contains Zerewitinoff active H-atoms are potentially capable of modifying polyisocyanates. (See, e.g.,WO 92/05212). Commercially available products suitable for this purpose contain NH_2 and/or NH groups as Zerewitinoff active H-atoms. Also available are compounds containing SH groups.

[0005] Alkoxysilanes containing SH groups are described, for example, in GB-A-1,102,251; EP-A-0,018,094; DE-A-1,162,818; U.S. Patent 3,590,065; U.S. Patent 3,849,471; U.S. Patent 4,082,790; U.S. Patent 4,012,403; and U.S. Patent 4,401,286. All alkoxysilanes containing SH groups have the unpleasant odor which is typical of mercaptans. The polymer may, therefore, have an unpleasant odor due to residues of these compounds.

[0006] α-Aminoalkyl silane derivatives which can be cross-linked by moisture may be prepared according to German Offenlegungsschriften Nos. 1,812,504 and 1,812,562. The functional silanes described here have, however, failed to achieve technical importance due to the complicated process for their synthesis.

[0007] Alkoxysilanes containing amino groups are described, e.g. in J. Org. Chem. 36 (1971), p. 3120; DE-A-1,152,695; DE-A-1,271,712; DE-A-2,161,716; DE-A-2,408,480; DE-A-2,521,399; DE-A-2,749,316; U.S. Patent 2,832,754; U.S. Patent 2,971,864; and U.S. Patent 4,481,364. Common to all amino-functional silanes known in the art is the disadvantage of being extremely reactive with isocyanates. Therefore, it is difficult to react these alkoxysilanes with polyisocyanates due to the incompatibility, inhomogeneity and extremely high viscosities of the reaction products.

[0008] Alkoxysilane-functional polyurethanes which crosslink via silane polycondensation are known (see „Adhesives Age"), 4/1995, p. 30 ff., for example). These alkoxysilane-terminated, moisture-curing, one-component polyurethanes are increasingly being used in the construction and car industries as flexible coating and sealing compounds and adhesives. Stringent demands regarding elongation, adhesive capacity and curing rate are required in these applications. In particular, the level of properties required by the car industry cannot be entirely achieved with currently available systems.

[0009] Alkoxysilane-functional polyurethanes which are prepared by the reaction of N-arylaminosilanes with NCO-prepolymers are known from EP-A 676,403. These products meet the car industry's requirements regarding their mechanical properties, for example, but the lack of thermal stability of the crosslinked polymers is a problem with the products. The reason for this deficiency is the known thermal instability of substituted, particularly aryl-substituted, ureas.

[0010] U.S. Patent 5,554,709 discloses that amino-functional silanes can be reacted with certain NCO prepolymers, provided that the functionality of the prepolymer is less than 2.

[0011] U.S. Patent 5,364,955 discloses that by initially reacting amino-functional silanes with maleic or fumaric acid esters to form secondary amino groups (i.e., aspartates), it is then possible to react these aspartates with NCO prepolymers without encountering incompatibility, inhomogeneity or extremely high viscosities in the reaction products. How-

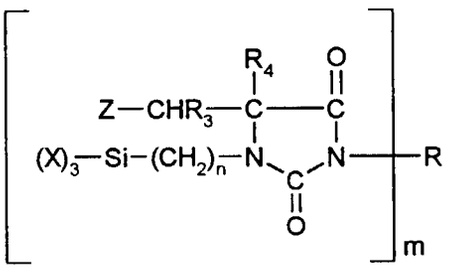
ever, this reference does not disclose that it is possible to react all types of polyisocyanates with aspartates, i.e., polyisocyanate monomers and polyisocyanate adducts are not disclosed.

[0012] It is an object of the present invention to provide compounds containing alkoxysilane groups that are liquid and do not suffer from the incompatibility, inhomogeneity and viscosity problems encountered with the prior art reaction products of isocyanates with alkoxysilanes containing NH groups. It is an additional object of the present invention to be able to prepare these compounds from any type of polyisocyanate, including polyisocyanate monomers, polyisocyanate adducts and NCO prepolymers. It is also an object of the present invention to provide compounds containing alkoxysilane group that can be cured by silane polycondensation to form coatings and adhesives.

[0013] These object may be achieved with the compounds containing alkoxysilane groups and hydantoin groups according to the present invention described hereinafter. These compounds are prepared by reacting polyisocyanates with aspartates (obtained by reacting aminoalkyl alkoxysilanes with maleic or fumaric acid esters) to form compounds containing urea groups and subsequently converting the urea groups to hydantoin groups.

Summary of the Invention

[0014] The present invention relates to compounds containing alkoxysilanes and hydantoin groups corresponding to the formula



(I)

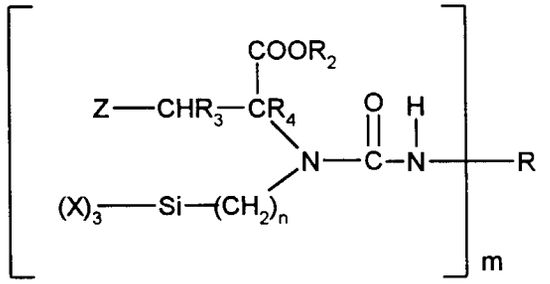
wherein

X	represents identical or different organic groups which are inert to isocyanate groups below 100°C, provided that at least one of these groups is an alkoxy group,
Z	represents $COOR_1$ or an aromatic ring,
R	represents the residue obtained by removing the isocyanate groups from an organic monomeric polyisocyanate or a polyisocyanate adduct of an NCO content from 5.1 to 60%,
R_1	represents an organic group which is inert to isocyanate groups at a temperature of 100°C or less,
R_3 and R_4	are identical or different and represent hydrogen or organic groups which are inert to isocyanate groups at a temperature of 100°C or less,
n	is an integer from 1 to 8 and
m	has an average value of 2 to 6.

[0015] The present invention also relates to the use of these compounds for the preparation of coatings and adhesives.

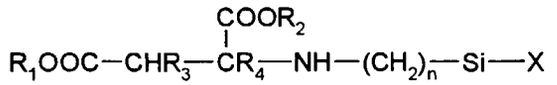
Detailed Description of the Invention

[0016] The compounds containing alkoxysilane groups and hydantoin groups of formula (1) are prepared by heating the corresponding compounds containing urea groups at elevated temperatures to convert the urea groups to hydantoin groups. The compounds containing urea groups correspond to formula (II)



(II)

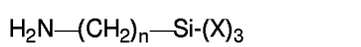
[0017] The compounds of formula (II) are prepared by reacting polyisocyanates with compounds containing alkoxysilane and aspartate groups (secondary amino groups) corresponding to the formula



(III)

to form compounds containing alkoxysilane and urea groups.

[0018] The compounds of formula (III) are prepared by reacting aminoalkyl alkoxysilanes corresponding to the formula



(IV)

with maleic, fumaric or cinnamic acid esters corresponding to the formula

(V)

[0019] In formulas I to V

X represents identical or different organic groups which are inert to isocyanate groups below 100°C, provided that at least one of these groups is an alkoxy group, preferably alkyl or alkoxy groups having 1 to 4 carbon atoms, more preferably alkoxy groups;

Z represents $COOR_1$ or an aromatic ring, preferably $COOR_1$,

R represents the residue obtained by removing the isocyanate groups from an organic monomeric polyisocyanate or a polyisocyanate adduct of an NCO content from 5.1 to 60%, preferably from 7% to 50%,

R_1 and R_2 are identical or different and represent organic groups which are inert to isocyanate groups at a temperature of 100°C or less, preferably alkyl groups having 1 to 8 carbon atoms, more preferably alkyl groups having 1 to 4 carbon atoms and most preferably methyl, ethyl or butyl groups,

R_3 and R_4 are identical or different and represent hydrogen or organic groups which are inert towards isocyanate groups at a temperature of 100°C or less, preferably hydrogen and

n is an integer from 1 to 8, preferably 2 to 4 and more preferably 3 and

m has an average value from 2 to 6 (the preferred values depend upon the type of residue R).

[0020] Especially preferred are compounds in which X represents methoxy, ethoxy groups or propoxy groups, more preferably methoxy or ethoxy groups and most preferably methoxy groups, and n is 3.

[0021] Examples of suitable aminoalkyl alkoxysilanes of formula (IV) include 2-aminoethyldimethylmethoxysilane; 6-

aminohexyltributoxysilane; 3-aminopropyl-trimethoxysilane; 3-aminopropyltriethoxysilane; 3-aminopropyl-methyldiethoxysilane; 5-aminopentyltrimethoxysilane; 5-aminopentyl-triethoxysilane and 3-aminopropyltriisopropoxysilane; 3-aminopropyl-trimethoxysilane and 3-aminopropyl-triethoxysilane are particularly preferred.

[0022] Examples of optionally substituted maleic, fumaric or cinnamic acid esters suitable for use in the preparation of the polyaspartates include dimethyl, diethyl, dibutyl (e.g., di-n-butyl), diamyl, di-2-ethylhexyl esters and mixed esters based on mixture of these and/or other alkyl groups of maleic acid and fumaric acid; the methyl, ethyl and butyl esters of cinnamic acid; and the corresponding maleic, fumaric and cinnamic acid esters substituted by methyl in the 2- and/or 3-position. The dimethyl esters of maleic acid are preferred and the diethyl and dibutyl esters are especially preferred.

[0023] The reaction of primary amines with maleic, fumaric or cinnamic acid esters to form the aspartates of formula (III) is known and described, e.g., in EP-A-0,403,921; DE-OS 1,670,812; and DE-OS 2,158,945. While none of these publications suggests the reaction of alkoxysilane-functional amines with maleic or fumaric acid esters, this reaction is described in U.S. Patent 5,364,955. The preparation of the aspartates may be carried out, for example, at a temperature of 0 to 100°C using the starting materials in such proportions that at least 1, preferably 1, olefinic double bond is present for each primary amino group. Excess starting materials may be removed by distillation alter the reaction. The reaction may be carried out with or without a solvent, but the use of a solvent is less preferred. If a solvent is used, dioxane is an example of a suitable solvent.

[0024] The compounds of formula (III) are colorless to pale yellow. They may be reacted with polyisocyanates to form the compounds of formula (II) without further purification.

[0025] Suitable polyisocyanates for preparing the compounds of formula (II) and ultimately formula (I) include monomeric diisocyanates, or polyisocyanate adducts having an average functionality of 2 to 6 and an NCO content of 5.1 to 60%, preferably 7% to 50%. The monomeric diisocyanates and polyisocyanate adducts have an average functionality of 2 to 6 and more preferably 2 to 4.

[0026] Suitable monomeric diisocyanates may be represented by the formula

$$R(NCO)_2$$

[0027] Diisocyanates suitable for the process according to the invention are those in which R represents a divalent aliphatic hydrocarbon group having 4 to 40, preferably 4 to 18 carbon atoms, a divalent cycloaliphatic hydrocarbon group having 5 to 15 carbon atoms, a divalent araliphatic hydrocarbon group having 7 to 15 carbon atoms or a divalent aromatic hydrocarbon group having 6 to 15 carbon atoms.

[0028] Examples of the suitable organic diisocyanates include 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2,2,4-trimethyl-1,6-hexamethylene diisocyanate, 1,12-dodecamethylene diisocyanate, cyclohexane-1,3- and -1,4-diisocyanate, 1-isocyanato-2-isocyanatomethyl-cyclopentane, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethyl-cyclohexane (isophorone diisocyanate or IPDI), bis-(4-isocyanatocyclohexyl)-methane, 2,4'-dicyclohexyl-methane diisocyanate, 1,3- and 1,4-bis-(isocyanatomethyl)-cyclohexane, bis-(4-isocyanato-3-methylcyclohexyl)-methane, $\alpha,\alpha,\alpha',\alpha'$-tetramethyl-1,3- and/or -1,4-xylylene diisocyanate, 1-isocyanato-1-methyl-4(3)-isocyanatomethyl cyclohexane, 2,4- and/or 2,6-hexahydrotoluylene diisocyanate, 1,3- and/or 1,4-phenylene diisocyanate, 2,4-diisocyanatotoluene (and mixtures thereof with preferably up to 35 wt.%, based on the mixture of 2,6-diisocyanatotoluene), 4,4'-diphenylmethane diisocyanate (and mixture thereof with 2,4'-diphenyl-methane diisocyanate and/or 2,2'-diphenylmethane diisocyanate), 1,5-diisocyanato naphthalene and mixtures thereof.

[0029] Polyisocyanates containing 3 or more isocyanate groups such as 4-isocyanatomethyl-1,8-octamethylene diisocyanate and aromatic polyisocyanates such as 4,4',4''-triphenylmethane triisocyanate and polyphenyl polymethylene polyisocyanates obtained by phosgenating aniline/formaldehyde condensates may also be used.

[0030] Preferred organic diisocyanates include 1,6-hexamethylene diisocyanate, 1-isocyanato-3-isocyanatomethyl-3,5,5-trimethylcyclohexane (isophorone diisocyanate or IPDI), bis-(4-isocyanatocyclohexyl)-methane, 1-isocyanato-1-methyl-4(3)-isocyanatomethyl cyclohexane, 2,4- and/or 2,6-toluylene diisocyanate, and 2,4- and/or 4,4'-diphenyl-methane diisocyanate.

[0031] In accordance with the present invention the polyisocyanate component may also be in the form of a polyisocyanate adduct. Suitable polyisocyanate adducts are those containing isocyanurate, uretdione, biuret, urethane, allophanate, carbodiimide and/or oxadiazine-trione groups. The polyisocyanates adducts have an NCO content of 5.1 to 30% by weight.

1) Isocyanurate group-containing polyisocyanates which may be prepared as set forth in DE-PS 2,616,416; EP-OS 3,765; EP-OS 10,589; EP-OS 47,452; US-PS 4,288,586 and US-PS 4,324,879.

The isocyanato-isocyanurates generally have an average NCO functionality of 3 to 4,5 and an NCO content of 10 to 25% and most preferably 15 to 25% by weight.

2) Uretdione diisocyanates which may be prepared by oligomerizing a portion of the isocyanate groups of a diiso-

cyanate in the presence of a suitable catalyst, e.g., a trialkyl phosphine catalyst, and which may be used in admixture with other aliphatic and/or cycloaliphatic polyisocyanates, particularly the isocyanurate group-containing polyisocyanates set forth under (1) above.

3) Biuret group-containing polyisocyanates which may be prepared according to the process disclosed in U.S. Patent Nos. 3,124,605; 3,358,010; 3,644,490; 3,862,973; 3,906,126; 3,903,127; 4,051,165; 4,147,714 or 4,220,749 by using co-reactants such as water, tertiary alcohols, primary and secondary monoamines, and primary and/or secondary diamines. These polyisocyanates preferably have an NCO content of 18 to 22% by weight and an average NCO functionality of 3 to 4.5.

4) Urethane group-containing polyisocyanates which may be prepared in accordance with the process disclosed in U.S. Patent No. 3,183,112 by reacting excess quantities of polyisocyanates, preferably diisocyanates, with low molecular weight glycols and polyols having molecular weights of less than 500, such as trimethylol propane, glycerine, 1,2-dihydroxy propane and mixtures thereof. The urethane group-containing polyisocyanates have a most preferred NCO content of 5.1 to 20% by weight, preferably 7 to 15% and an (average) NCO functionality of 2.5 to 4.

5) Allophanate group-containing polyisocyanates which may be prepared according to the processes disclosed in U.S. Patent Nos. 3,769,318; 4,160,080 and 4,177,342. The allophanate group-containing polyisocyanates have a most preferred NCO content of 12 to 21% by weight and an (average) NCO functionality of 2 to 4.5.

6) Isocyanurate and allophanate group-containing polyisocyanates which may be prepared in accordance with the processes set forth in U.S. Patents 5,124,427; 5,208,334 and 5,235,018, the disclosures of which are herein incorporated by reference, preferably polyisocyanates containing these groups in a ratio of monoisocyanurate groups to monoallophanate groups of about 10:1 to 1:10, preferably about 5:1 to 1:7.

7) Carbodiimide group-containing polyisocyanates which may be prepared by oligomerizing di- or polyisocyanates in the presence of known carbodiimidization catalysts as described in DE-PS 1,092,007; US-PS 3,152,162 and DE-OS 2,504,400, 2,537,685 and 2,552,350.

8) Polyisocyanates containing oxadiazinetrione groups and containing the reaction product of two moles of a diisocyanate and one mole of carbon dioxide.

Preferred polyisocyanate adducts are the polyisocyanates containing isocyanurate groups, biuret groups, allophanate gorups and/or uretdione groups.

[0032] The compounds of formula (I) containing alkoxysilane groups and hydantoin groups are prepared by reacting the polyisocyanates with the compounds of formula (III) at an equivalent ratio of aspartate groups (i.e., secondary amino groups) to isocyanate groups of approximately 1:1. The reaction is preferably carried out by incrementally adding the aspartate to the polyisocyanate. The reaction to form the urea group-containing intermediate is conducted at a temperature of 10 to 100°C, preferably 20 to 80°C and more preferably 20 to 50°C. After this addition reaction is complete the temperature is increased to 60 to 240°C, preferably 80 to 160°C and more preferably 100 to 140°C, to convert the urea groups to hydantoin groups with the elimination of a monoalcohol.

[0033] Instead of forming the urea groups and hydantoin groups in two steps, the reaction may be carried out entirely at elevated temperatures in order to form the urea groups and hydantoin groups in one step. When conducting the reaction in one step, care must be taken to avoid the reaction between monoalcohols (which are obtained as a by-product during the formation of hydantoins) with isocyanate groups that have not been converted to urea groups. In either the one or two step process the conversion of urea groups to hydantoin groups may be carried out in the presence of catalysts, such as carboxylic acids, to reduce the temperature and/or the reaction time needed for this conversion.

[0034] The compounds of the present invention are suitable for the production of coating or adhesive compositions which can be cross-linked by „silane polycondensation," i.e,. the condensation of silane groups (Si-OR) to form siloxane groups (Si-O-Si). When used for this purpose, these compounds may be used as mixture with suitable acidic or basic catalysts. Examples include acids such as paratoluene sulfonic acid metallic salts such as dibutyl tin dilaurate; tertiary amines such as triethylamine or triethylene diamine; and mixtures of these catalysts. Low molecular weight, basic aminoalkyl trialkoxysilanes, such as those represented by formula (IV), also accelerate hardening of the compounds according to the invention.

[0035] The compounds of the present invention having alkoxysilane and hydantoin groups are valuable binders for the manufacture of coatings and adhesives which crosslink via a silane polycondensation in the presence of atmospheric moisture.

[0036] To manufacture these coatings and adhesives, the compounds having alkoxysilane and hydantoin groups are

optionally mixed with additives, solvents, fillers, pigments, adjuvants, thixotropic agents, catalysts, according to known technology.

[0037] The invention is further illustrated but is not intended to be limited by the following examples in which all parts and percentages are by weight unless otherwise specified.

EXAMPLES

Polyisocyanate 1

[0038] An isocyanurate group-containing polyisocyanate prepared from 1,6-hexamethylene diisocyanate and having an isocyanate content of 21.6%, a content of monomeric diisocyanate of <0.2% and a viscosity at 20°C of 3000 mPa.s (available from Bayer Corporation as Desmodur N 3300).

Polyisocyanate 2

[0039] An isocyanurate group-containing polyisocyanate prepared from 1,6-hexamethylene diisocyanate and having an isocyanate content of 23%, a content of monomeric diisocyanate of <0.2% and a viscosity at 25°C of 1200 mPa.s (available from Bayer Corporation as Desmodur XP-7014).

Polyisocyanate 3

[0040] A polyisocyanate which contains allophanate groups and isocyanurate groups, is prepared from 1,6-hexamethylene diisocyanate and has an isocyanate content of 19%, a content of monomeric diisocyanate of <0.2% and a viscosity at 25°C of about 270 mPa.s (available from Bayer Corporation as Desmodur XP-7040).

Polyisocyanate 4

[0041] A polyisocyanate which contains allophanate groups and isocyanurate groups, is prepared from 1,6-hexamethylene diisocyanate and has an isocyanate content of 21.4%, a monoallophanate group content of 11%, a content of monomeric diisocyanate of <0.2% and a viscosity at 25°C of about 1200 mPa.s (available from Bayer Corporation as Desmodur XP-7100).

Polyisocyanate 5

[0042] A mixture containing 70 parts by weight of a uretdione group-containing polyisocyanate, i.e., dimerized 1,6-hexamethylene diisocyanate and 30 parts by weight of N,N',N"-tris-(6-isocyanatohexyl)-isocyanurate together with minor quantities of higher homologs of both products and having an average viscosity of 150 mPa.s at 23°C and an average NCO content of 22.5% (available from Bayer Corporation as Desmodur N 3400).

Polyisocyanate 6

[0043] A mixture of diphenylmethane diisocyanate isomers as well as their higher homologs, obtained by phosgenation of an aniline/formaldehyde condensation product having an NCO content of about 31% and a viscosity of about 40 mPa.s (available from Bayer Corporation as Mondur MRS-4).

Polyisocyanate 7

[0044] A biuret group-containing polyisocyanate prepared from 1,6-hexamethylene diisocyanate and having an isocyanate content of about 23%, a content of monomeric diisocyanate of <0.7% and a viscosity at 25°C of 1300-2200 mPa.s (available from Bayer Corporation as Desmodur N 3200).

Silane Aspartates - General Procedure

[0045] 8.27 equiv of 3-aminopropyltrialkoxysilane were added to a 5 liter flask fitted with agitator, thermocouple, nitrogen inlet and addition tunnel with condenser. 8.27 equiv of dialkyl maleate were added dropwise over a period of 2 hours. The temperature of the reactor was maintained at 25°C during the addition. The reactor was maintained at 25°C for an additional 5 hours at which time the product was poured into glass containers and sealed under a blanket of nitrogen. After one week the unsaturation number was 0.6 indicating the reaction was ~99% complete.

[0046] The following compounds were prepared:

	Viscosity at 25°C
N-(3-triethoxysilylpropyl) aspartic acid diethyl ester	9 mPa.s
N-(3-triethoxysilylpropyl) aspartic acid dibutyl ester	11 mPa.s
N-(3-trimethoxysilylpropyl) aspartic acid diethyl ester	11 mPa.s
N-(3-trimethoxysilylpropyl) aspartic acid dibutyl ester	18 mPa.s

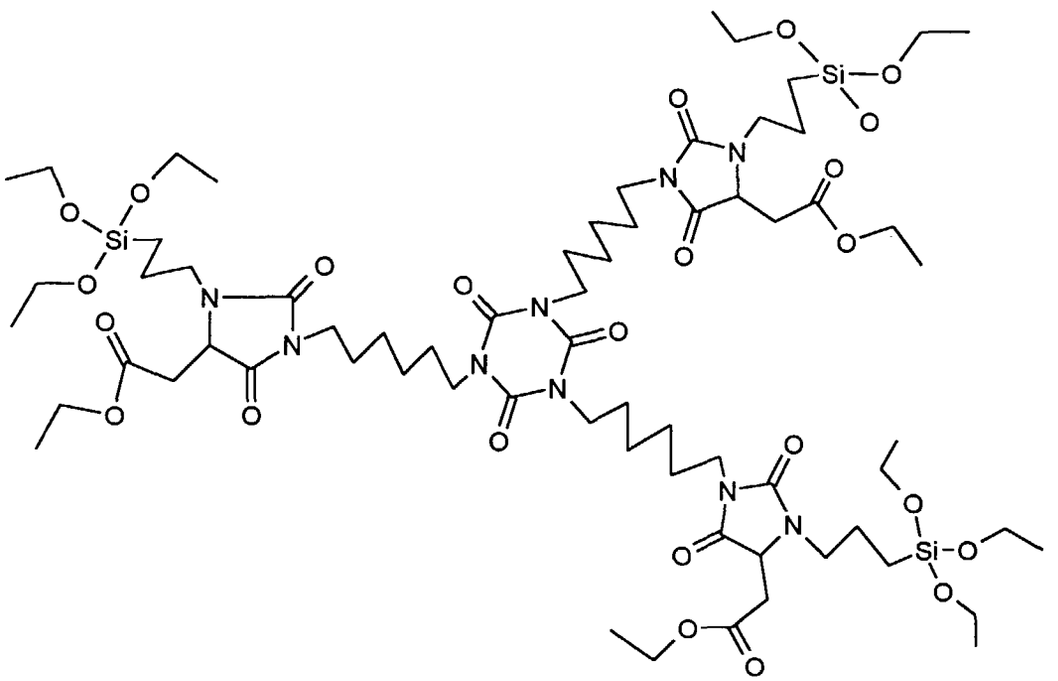
Alkoxysilane Resin 1

[0047] Tris-[3-(trimethoxysilyl)propyl]-isocyanurate (Silquest Y-11597, available from Witco Corp.).

Example 1

[0048] 669.0 parts (1.7 equiv) of N-(3-triethoxysilylpropyl) aspartic acid diethyl ester and 331 parts (1.7 equiv) of polyisocyanate 1 were added to a three neck, 5 liter, round bottom flask equipped with an agitator, nitrogen inlet, thermocouple and condenser. The reaction to form the urea was accompanied by an exotherm which increased the temperature of the reaction mixture to 80°C. The reaction was held at 80°C for 14 hours at which time the IR spectrum showed no residual isocyanate in the urea. The product was determined to be >300,000 at 25°C.

[0049] 500 parts of the urea were combined with 5 parts of glacial acetic acid in a 1 liter flask fitted with an agitator, nitrogen inlet, thermocouple and condenser with vacuum outlet. The reaction temperature was increased to 106°C where the reaction mixture began to reflux as ethanol was released from the cyclization reaction. When the IR spectrum showed no residual urea, the reactor was cooled to 75°C and a vacuum was applied at 1 torr. 38.8 parts of ethanol (theoretical 40.8 parts) were isolated. The product yield was 463 parts. The product has viscosity of >101,000 mPa.s at 25°C. Analysis via GC, IR NMR and GPC were consistent with the following structure:



Examples 2-16

[0050] Example 1 was repeated with the exception that Polyisocyanate 1 was replaced with an equivalent amount of Polyisocyanates 2-7 and also with 1,6-hexamethylene diisocyanate (HDI), isophorone diisocyanate (IPDI) and bis-(4-isocyanatocyclohexyl) methane (HMDI). In addition, the aspartate reacted with the polyisocyanate was also varied as set forth in Table 1, The viscosities of the resulting products containing alkoxysilane groups and hydantoin groups are set forth in Table 1.

Table 1

Example No.	Polyisocyanate	Trialkoxy Silane	Dialkyl Maleate	Viscosity of Hydantoin (mPa.s at 25°C)
1	Polyisocyanate 1	Ethoxy	Ethyl	101,000
2	Polyisocyanate 1	Methoxy	Ethyl	
3	Polyisocyanate 2	Ethoxy	Ethyl	86,700
4	Polyisocyanate 3	Ethoxy	Ethyl	22,300
5	Polyisocyanate 4	Ethoxy	Ethyl	57,700
6	Polyisocyanate 5	Ethoxy	Ethyl	59,200
7	Polyisocyanate 5	Methoxy	Ethyl	24,300
8	Polyisocyanate 6	Methoxy	Ethyl	>300,000
9	Polyisocyanate 7	Ethoxy	Ethyl	118,000
10	HDI	Ethoxy	Ethyl	23,300
11	HDI	Methoxy	Ethyl	1200
12	HDI	Ethoxy	Butyl	950
13	IPDI	Methoxy	Butyl	780
14	IPDI	Ethoxy	Ethyl	132,000
15	IPDI	Methoxy	Ethyl	>300,000
16	HMDI	Methoxy	Ethyl	>300,000

Examples 17-20 Preparation of coatings from the urea and hydantoin group-containing compounds of Example 1

[0051] Coatings were prepared from the urea group-containing and the corresponding hydantoin group-containing compounds prepared in Example 1. In addition to these compounds the coating compositions contained the ingredients set forth in Table 2. The levelling agent was Byk 358, a silicone based additive, available form Byk Chemie; the catalyst was dibutyl tin dilaurate. The properties of the resulting coatings are also set forth in Table 2.

Table 2

Example		17	18	19	20
Ingredient					
Urea from Ex.		200	0	100	0
Hydantoin from Ex. 1		0	200	0	100
Alkoxysilane Resin 1		0	0	100	100
Ethanol		200	200	200	200
Levelling Agent		1	1	1	1
Catalyst		2	2	2	2
Pendulum Hardness, sec.					
Day	1	0	0	0	0
	4	13	15	61	55
	10	39	52	123	87
	26	178	181	193	171
Pencil Hardness, Day 26		2B	2B	3H	2H
MEK Double Rubs					
Day	1	wet	wet	wet	wet
	4	1	4	70	40
	10	25	32	100	100
	26	100	100	100	100
Chemical Spot Test:1,4 and 24 hour spot					
Gasoline		ne,s,s	ne,s,s	ne,ne,ne	ne,ne,ne
Motor oil		ne,ne,ne,	ne,ne,ne	ne,ne,ne,	ne,ne,ne
Methyl ethyl ketone		ds,ds,ds,	ds,ds,ds,	ne,ne,ne	ne,ne,ne
Isopropanol		s,s,s,	s,s,s,	ne,ne,ne	ne,ne,ne
Propylene glycol methyl ether acetate		s,s,ds	s,ds,ds,	ne,ne,ne	ne,ne,ne
HCl, 37%		ne,st,bl	ne,st,bl	ne,st,ds	ne,st,ds
H_2SO_4, 50%		ne,ne,ne	ne,ne,ne	ne,ne,st	ne,ne,st
Acetic acid		ds,ds,ds	ds,ds,ds	s,ds,ds	s,ds,ds
Aniline		ds,ds,ds,	ds,ds,ds	s,ds,ds	s,ds,ds
Tg, °C		59	51	61	69

[0052] MEK double rubs was determined by wetting a cloth with methyl ethyl ketone and then rubbing each panel up to 100 times. A double rub consists of one back and forth rub against the coated panel. Values of less than 100 indicate the number of double rubs before the coatings was destroyed.

[0053] Pendulum hardness was determined in accordance with ASTM D-4366-87 (Koenig Pendulum Hardness).

[0054] Chemical spot resistance was determined by placing a drop of the particular liquid on a coated panel and covering it with a 4 oz. glass jar. For those solvents that rapidly evaporate a cotton ball was placed on the coated panel liquids and kept saturated. Alter the appropriate time interval, the coated panels were washed, evaluated to determine the effect of the liquid, and assigned one of the following classifications:

ne No effect

s Film softened, but recovered after 1 hour
ds Dissolved
st Stained
bl Blistered

Examples 21 - 25

[0055] Coating compositions were prepared by adding 1 part of dibutyl tin dilaurate to 100 parts (70% solids) of the hydantoin group-containing compound of Example 1, to alkoxysilane resin 1 or to mixture thereof as set forth in Table 3. The resins were present as a 70% solution in toluene. The compositions were applied to steel panels at a wet film thickness of 5 mils (3.5 mils dry film thickness). The properties of the resulting coatings are set forth in Table 3.

Table 3

Example	21	22	23	24	25
Components					
Hydantoin from Ex.1	0	25	50	75	100
Alkoxysilane Resin 1	100	75	50	25	0
Coating Properties					
Pendulum Hardness, secs					
1 day	148	57	32	5	0
3 days	169	102	52	10	10
16 days	184	145	101	52	81
25 days	183	153	127	94	98
MEK, double rubs					
1 day	100	10	2	1	1
2 days	days 100	100soft	10	1	1
16 days	100	100	100	100	100 soft
Film appearance	cracked, curled	smooth, glossy	smooth glossy	smooth glossy	smooth glossy
Chemical Spot Test: 1,4 and 24 hours spots					
Gasoline	--	ne,ne,ne	ne,ne,ne	ne,s,ds	s,s,ds
Motor oil	--	ne,ne,ne	ne,ne,ne	ne,ne,ne	ne,ne,ne
Methyl ethyl ketone	--	s,s,ds	ne,s,s	ne,s,ds	ds,ds,ds
Isopropanol	--	ne,s,s,	ne,s,s	ne,s,s	s,s,s
Propylene glycol methyl ether acetate	--	ne,ne,ne	ne,ne,ne	ne,ne,ne	ne,ne,ne
HCl, 37%	--	s,ds,ds	s,s,st	ne,st,ds	ne,ne,ne
H_2SO_4, 50%	--	ne,ne,ne	ne,ne,ne	ne,ne,ne	ne,ne,ne
Acetic acid	--	ne,ds,ds,	ds,ds,ds,	ds,ds,ds	ds,ds,ds
Aniline	--	ne,st,st	ne,ds,ds	s,ds,ds	ds,ds,ds

Examples 22-24

[0056] Demonstrate the ability of the compounds containing hydantoin groups to flexibilize other silane containing compounds that are not capable of forming films on their own.

Examples 26-35

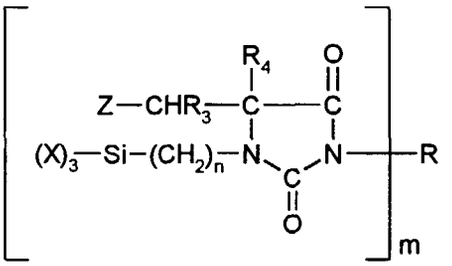
[0057] Coatings were prepared from the hydantoin group-containing compounds and additional ingredients set forth in Table 4. The levelling agent was Byk 358, a silicone based additive, available from Byk Chemie; the catalysts were dibutyl tin dilaurate (DBTDL) and paratoluene sulfonic acid (PTSA). The properties of the resulting coating are also set forth in Table 4.

Table 4

Example	**26**	**27**	**28**	**29**	**30**	**31**	**32**	**33**	**43**	**35**
Ingredients										
Hydantoin from										
Ex.1	20	0	0	0	0	10	0	0	0	0
Ex.7	0	20	0	0	0	0	10	0	0	0
Ex.8	0	0	20	0	0	0	0	0	0	0
Ex.2	0	0	0	20	0	0	0	0	0	0
Ex.3	0	0	0	20	20	0	0	0	0	0
Alkoxysilane resin 1	0	0	0	0	0	10	10	10	10	10
Levelling agent	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1	0.1
Ethanol	20	20	20	20	20	20	20	20	20	20
PtSA	0.5	0.5	0.5	0.5	0.5	0.35	0.35	0.35	0.35	0.35
DBTL	0	0	0	0	0	0.35	0.35	0.35	0.35	0.35
Pencil hardness, sec.										
Day 4	2H	2H	3H	shattered	2H	H	F	2B	2H	F
Day 7	3H	2H	3H	--	2H	3H	F	2B	2H	F
Day 7	3H	3H	3H	--	2H	2H	2H	HB	2H	2H
Pendulum Hardness, sec										
Day 4	190	196	167	0	168	63	132	90	158	116
Day 7	195	197	154	0	182	84	155	101	168	129
Day 14	189	161	245	0	168	81	85	155	160	122

Claims

1. A compound containing alkoxysilane and hydantoin groups and corresponding to the formula



(I)

wherein

X	represents identical or different organic groups which are inert to isocyanate groups below 100°C, provided that at least one of these groups is an alkoxy group,
Z	represents $COOR_1$ or an aromatic ring,
R	represents the residue obtained by removing the isocyanate groups from an organic monomeric polyisocyanate or a polyisocyanate adduct of an NCO content from 5,1 to 60%,
R_1	represents an organic group which is inert to isocyanate groups at a temperature of 100°C or less.
R_3 and R_4	are identical or different and represent hydrogen or organic groups which are inert to isocyanate groups at a temperature of 100°C or less,
n	is an integer of 100°C or less,
m	has an average value of 2 to 6.

2. The compound of Claim 1 wherein

X	represents identical or different alkyl or alkoxy groups having 1 to 4 carbon atoms,
Z	represents $COOR_1$,
R_1	is an alkyl group having 1 to 8 carbon atoms,
R_3 and R_4	represents hydrogen and
n	is an integer from 2 to 4.

3. The compound of Claim 1 wherein

X	represents identical or different alkoxy groups having 1 to 4 carbon atoms,
Z	represents $COOR_1$,
R_1	is methyl, ethyl or butyl,
R_3 and R_4	represent hydrogen and
n	is 3.

4. The compound of Claim 1 wherein R represents the residue obtained by removing the isocyanate groups from an organic monomeric polyisocyanate.

5. The compound of Claim 2 wherein R represents the residue obtained by removing the isocyanate groups from an organic monomeric polyisocyanate.

6. The compound of Claim 3 wherein R represents the residue obtained by removing the isocyanate groups from an organic monomeric polyisocyanate.

7. The compound of Claim 1 wherein R represents the residue obtained by removing the isocyanate groups from a polyisocyanate adduct.

8. The compound of Claim 2 wherein R represents the residue obtained by removing the isocyanate groups from a polyisocyanate adduct.

9. The compound of Claim 3 wherein R represents the residue obtained by removing the isocyanate groups from a polyisocyanate adduct.

10. The compound of Claim 1 wherein R represents the residue obtained by removing the isocyanate groups from a polyisocyanate containing isocyanurate groups, biuret groups, allophanate groups and/or uretdione groups.

11. The compound of Claim 2 wherein R represents the residue obtained by removing the isocyanate groups from a polyisocyanate containing isocyanurate groups, biuret groups, allophanate groups and/or uretdione groups.

12. The compound of Claim 3 wherein R represents the residue obtained by removing the isocyanate groups from a polyisocyanate containing isocyanurate groups, biuret groups, allophanate groups and/or uretdione groups.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 11 8191

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	EP 0 031 996 A (M & T CHEMICALS, INC.) * the whole document *	1-12	C07F7/18
D,A	US 5 364 955 A (ZWIENER, C. ET AL.) * the whole document *	1	
A	DE 16 70 812 A (BAYER AG) * the whole document *	1	
E	EP 0 807 649 A (BAYER AG) * the whole document *	1-12	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C07F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	4 March 1998	Rinkel, L

CATEGORY OF CITED DOCUMENTS

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